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(54) SUBSTRATE OF A CERAMIC MATERIAL

SUBSTRAT AUS EINEM KERAMISCHEN MATERIAL

SUBSTRATS EN CERAMIQUE

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Description

The invention relates to a substrate made from a ceramic material. The invention also relates to a ceramic material and to methods of manufacturing such a ceramic material.

Substrates made from a ceramic material are known *per se*. They are generally composed of a thin sheet of sintered ceramic material, such as the binary compounds aluminium oxide (Al_2O_3), magnesium oxide (MgO), beryllium oxide (BeO), aluminium nitride (AlN) or silicon carbide (SiC). Substrates made from compounds, such as MgSiN_2 , are also known. Because of their satisfactory electrically insulating properties, said known substrates are used in passive and active electrical components, such as resistors, capacitors, transformers and power transistors. In these applications, they serve as supports of current-conducting structures. In Patent Application US 5.411.924, filed by Applicant, the advantages and disadvantages of a number of substrates are briefly stated.

An important field of application of ceramic substrates is formed by the Si-semiconductor technology. Substrates suitable for said technology must have a high electrical resistance R (ohm), a satisfactory strength σ (MPa) and a high thermal conductance k (W/m.K). In addition, the coefficient of expansion α ($1/\text{K}$) of the substrates should be substantially equal to that of Si. Said last-mentioned measure ensures that Si structures provided on the substrate do not crack and/or become detached under the influence of variations in temperature. The coefficient of expansion of silicon is approximately $4.8 \cdot 10^{-6} \text{K}^{-1}$.

As a result of said requirements, the use of magnesium oxide and aluminium oxide as the substrate material is not optimal because their thermal conductance is too low and their coefficient of expansion is too high. Said disadvantages apply in particular when these substrates are used in large Si-semiconductor structures and/or "power devices". The coefficient of expansion of MgSiN_2 ($5.8 \cdot 10^{-6} \text{K}^{-1}$) is much closer to that of Si than that of aluminium oxide and magnesium oxide. However, particularly in the case of relatively large substrate surfaces of MgSiN_2 , on which complex semiconductor structures are provided, the difference between the coefficients of expansion of Si and MgSiN_2 is still too large. Ceramic substrates of silicon carbide are relatively expensive because this material is difficult to process. In addition, silicon carbide has a relatively high dielectric constant. As a result, this material is less suitable for use as a substrate in electronic components. Ceramic bodies of beryllium oxide have the important disadvantage that they comprise toxic beryllium. Substrates of aluminium nitride exhibit a favourable, high thermal conductance (approximately 150 W/m.K) and a coefficient of expansion ($4.8 \cdot 10^{-6} \text{K}^{-1}$) which is substantially identical to that of Si. However, this material is difficult to manufacture and hence relatively expensive.

It is an object of the invention to provide a substrate of a ceramic material which does not have the above-mentioned disadvantages. The invention more particularly aims at providing a ceramic substrate which has a relatively high thermal conductance, a coefficient of expansion substantially equal to that of Si and which can be manufactured relatively easily and hence at low cost.

These and other objects of the invention are achieved by a substrate of a ceramic material which is characterized in accordance with the invention in that the material comprises 44-47 at.% Al, 31-39 at.% O, 8-13 at.% C and 8-12 at.% N.

It has been found that a ceramic substrate whose composition is in accordance with the invention has substantially ideal properties for use in the Si-semiconductor technology. For example, the coefficient of expansion of the inventive substrate material is equal to that of Si, namely $4.8 \cdot 10^{-6} \text{K}^{-1}$. In addition, the theoretical thermal conductance at 300 K is approximately 120 W/m.K. Further, the strength of the material is 295 MPa. These data show that the material has approximately the same favourable properties as AlN. Substrates in accordance with the invention, however, are much simpler and hence much cheaper to manufacture.

Experiments leading to the invention have shown that substantially single phase material can only be obtained within the above-mentioned composition range. Compositions outside said range generally comprise considerable quantities of other phases, such as aluminium oxide, aluminium oxynitride and/or aluminium oxycarbide. The presence of such foreign phases causes unfavourable properties, such as a substantial reduction of the thermal conductance. It is noted that a small part (up to 10 at. %) of Al can be replaced by B without this leading to a drastic change of the structure and properties of the inventive substrate.

The composition of the main component of the inventive substrate preferably corresponds to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. The above-mentioned properties regarding thermal conductance, coefficient of expansion and strength are found to be optimal in substrates of this material composition. It is noted that the error in the element analysis of said composition is approximately 1 at. % per element. It is further noted that the composition formula is based on the crystal structure of the inventive material. The overall composition may differ slightly from the composition based on the crystal structure. This may be caused by the fact that the glass phase of the ceramic material differs from the crystalline phase. The glass phase is situated between the crystalline grains. The expression "main component" is to be understood to mean herein the crystalline phase of the material.

The invention also relates to a ceramic material. In accordance with the invention, this material is characterized in that it comprises 44-47 at.% Al, 31-39 at. % O, 8-13 at.% C and 8-12 at. % N. Preferably, the composition of the main component of the material corre-

sponds to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. The ceramic material in accordance with the invention may be in the form of a moulding or a powder.

The invention also relates to a method of manufacturing a ceramic material. A first embodiment is characterized in that the method comprises the following steps

- a) pre-firing a mixture of Al_2O_3 , Al_4C_3 and AlN in a ratio based on the intended composition of the ceramic material,
- b) grinding the pre-fired product thus formed into a powder,
- c) sintering the powder to form a ceramic material.

By means of the inventive method, a substantially monophase material is obtained which comprises 44-47 at.% Al, 31-39 at.% O, 8-13 at.% C and 8-12 at.% N. Pre-firing preferably takes place in the temperature range between 1500 and 1700°C, and sintering preferably takes place in the temperature range between 1700 and 1900°C. Under these conditions, the quantity of foreign-phase material is less than 20 wt.%.

A second embodiment of the inventive method is characterized in that a mixture of Al_2O_3 , Al_4C_3 and AlN , in a ratio based on the intended composition of the ceramic material, is sintered under pressure to form said ceramic material. This method is commonly referred to as reactive sintering. In this method, pre-firing and grinding of the pre-fired product formed are dispensed with.

These and other aspects of the invention will be apparent from and elucidated with reference to the embodiments described hereinafter.

In the drawings:

Fig. 1 shows a substrate of a ceramic material in accordance with the invention,

Fig. 2 shows an X-ray diffraction pattern of the ceramic material in accordance with the invention.

In Fig. 1, reference numeral (1) refers to a flat substrate of a ceramic material. The dimensions of this substrate are 40 x 60 x 4 mm³. The composition of the main component of this ceramic material corresponds to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. The substrate was manufactured as described hereinbelow.

The starting materials used were powders of Al_2O_3 (CR-56, Baikowski), Al_4C_3 (WI, Cerac) and AlN (Tokuyoma Soda, F-Grade). These starting materials were used to prepare a mixture comprising 57.2 wt.% aluminium oxide, 23.1 wt.% aluminium carbide and 19.7 wt.% aluminium nitride. This powder mixture was compressed into pellets under a pressure of 5 MPa, said pellets were subsequently pre-fired at a temperature ranging between 1600 and 1650°C. The heating and cooling rates were 10°C per minute. After pre-firing of the pellets, they were ground into a powder having an average grain size of approximately 2 micrometers. Said powder was of a white colour.

An X-ray diffraction pattern was recorded of the powder thus manufactured, as shown in Fig. 2. In said figure, the intensity (random unit) of the radiation measured is plotted as a function of 2θ (°). The pattern was recorded by means of a Philips PW1800 diffractometer, while using monochromatic Cu-K α radiation. All the lines of the pattern can be assigned to a rhombohedral structure (R-3m, #166, wherein $a = 5.459 \text{ \AA}$ and $c = 14.952 \text{ \AA}$). This diamond-like structure explains why the material in accordance with the invention has a relatively high heat conductance. It could be derived from this diffraction pattern that the quantity of foreign-phase material is less than 5 wt. %. Element analysis showed that the composition of the ceramic material manufactured corresponded to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. The error in the element analysis is maximally 1 at.%.

The powdered ceramic material having this optimum chemical composition was used to manufacture substrates by means of hot pressing. In this process, approximately 10 g of the powder was pressed by means of a hot-pressing apparatus (HP20, supplier Thermal Technology Ind) to form a flat substrate. The hot-pressed powder was sintered at a pressure of 75 MPa for 3 hours at 1800°C. The heating and cooling rates were 10°C per minute. After the hot-pressing operation, the substrate was subjected to a number of measurements. The density of the substrate was 97%. The heat conductance of this substrate was found to be above 20 W/m.K. Calculations revealed that the theoretical heat conductance is approximately 141 W/m.K. This can be achieved by optimizing the sintering process. The average coefficient of expansion of the substrate thus manufactured was $4.8 \cdot 10^{-6} \text{ K}^{-1}$. The strength of the material was 295 MPa.

In further experiments, the above-mentioned aluminium oxide, aluminium oxycarbide and aluminium nitride were mixed and, immediately afterwards, subjected to a sintering treatment at an increased pressure for 3 hours at 1880-1900°C. The density of the material obtained ranges between 2.97 and 3.01 g/cm³. A favourable aspect of this so-called "reactive hot sintering method" is that the time-consuming pre-firing step as well as the grinding step can be dispensed with. In this manner, substrates or other mouldings can be manufactured rapidly and at low cost.

In still further experiments, a number of ceramic powders were manufactured, in which the quantity of the various elements of the ceramic material was varied around the above-mentioned optimum composition. Also of these powders an X-ray diffraction pattern was recorded under the same conditions as described hereinabove. The quantity of different-phase material was estimated by means of the surface area of non-assignable peaks. The chemical composition and the corresponding quantity of single phase material (pure phase) are listed in the Table

	Composition	pure phase (%)
1.	$\text{Al}_{48}\text{O}_{29}\text{C}_{14}\text{N}_9$	60
2.	$\text{Al}_{47}\text{O}_{31}\text{C}_{13}\text{N}_9$	80
3.	$\text{Al}_{46}\text{O}_{35}\text{C}_{11}\text{N}_{10}$	95
4.	$\text{Al}_{46}\text{O}_{36}\text{C}_{10}\text{N}_9$	98
5.	$\text{Al}_{46}\text{O}_{37}\text{C}_{10}\text{N}_{10}$	90
6.	$\text{Al}_{44}\text{O}_{39}\text{C}_8\text{N}_{11}$	80
7.	$\text{Al}_{43}\text{O}_{40}\text{C}_7\text{N}_{11}$	30

The ceramic materials in accordance with exemplary embodiments 1 and 7 are not in accordance with the invention. The ceramic materials in accordance with exemplary embodiments 2-6 are in accordance with the invention. The Table clearly shows that a single phase material is obtained if the ceramic material in accordance with the invention comprises 44-47 at. % Al, 31-39 at. % O, 8-13 at. % C and 8-12 at. % N.

In summary, the invention relates to a substrate made from a novel type of ceramic material. Said material comprises 44-47 at. % Al, 31-39 at. % O, 8-13 at. % C and 8-12 at. % N. Substrates made from this material exhibit a relatively high thermal conductance, a relatively great strength and their coefficient of expansion is equal to that of Si. Consequently, the substrates in accordance with the invention are very suitable for use in the Si-semiconductor technology. The main component of the ceramic material of the substrates preferably corresponds to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$. The invention also provides methods of manufacturing substrates and other mouldings from this material.

Claims

1. A substrate of a ceramic material, characterized in that said material comprises 44-47 at. % Al, 31-39 at. % O, 8-13 at. % C and 8-12 at. % N.
2. A substrate as claimed in Claim 1, characterized in that the composition of the main component of the material corresponds to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$.
3. A ceramic material, characterized in that said material comprises 44-47 at. % Al, 31-39 at. % O, 8-13 at. % C and 8-12 at. % N.
4. A ceramic material as claimed in Claim 3, characterized in that the composition of the main component of the material corresponds to the formula $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$.
5. A method of manufacturing a ceramic material as claimed in Claim 3 or 4, characterized in that the

method comprises the following steps

- a) pre-firing a mixture of Al_2O_3 , Al_4C_3 and AlN in a ratio based on the intended composition of the ceramic material,
 - b) grinding the pre-fired product into a powder,
 - c) sintering the powder to form a ceramic material.
6. A method as claimed in Claim 5, characterized in that pre-firing takes place in the temperature range between 1500 and 1700°C and in that sintering takes place in the temperature range between 1700 and 1900°C.
 7. A method of manufacturing a ceramic material as claimed in Claim 3 or 4, characterized in that a mixture of Al_2O_3 , Al_4C_3 and AlN, in a ratio based on the intended composition of the ceramic material, is sintered under pressure to form said ceramic material.

Patentansprüche

1. Substrat aus keramischem Material, dadurch gekennzeichnet, daß das Material 44 - 47 Atomprozent Al, 31 - 39 Atomprozent O, 8 - 13 Atomprozent C und 8 - 12 Atomprozent N enthält.
2. Substrat nach Anspruch 1, dadurch gekennzeichnet, daß die Zusammensetzung des Hauptanteils des Materials der Formel $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$ entspricht.
3. Keramisches Material, dadurch gekennzeichnet, daß das Material 44 - 47 Atomprozent Al, 31 - 39 Atomprozent O, 8 - 13 Atomprozent C und 8 - 12 Atomprozent N enthält.
4. Keramisches Material nach Anspruch 3, dadurch gekennzeichnet, daß die Zusammensetzung des Hauptanteils des Materials der Formel $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$ entspricht.
5. Verfahren zum Herstellen eines keramischen Materials nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß das Verfahren die nachfolgenden Verfahrensschritte umfaßt:
 - a) das Vorbrennen eines Gemisches aus Al_2O_3 , Al_4C_3 und AlN in einem Verhältnis, das auf der beabsichtigten Zusammensetzung des keramischen Materials gründet,
 - b) das Zerpulvern des vorgebildeten Erzeugnisses,
 - c) das Sintern des Pulvers zu einem keramischen Material.
6. Verfahren nach Anspruch 5, dadurch gekennzeichnet,

net, daß der Vorbrennvorgang in dem Temperaturbereich zwischen 1500 und 1700°C erfolgt und daß der Sintervorgang in einem Temperaturbereich zwischen 1700 und 1900°C durchgeführt wird.

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7. Verfahren zum hersteilen eines keramischen Materials nach Anspruch 3 oder 4, dadurch gekennzeichnet, daß ein Gemisch aus Al_2O_3 , Al_4C_3 und AlN in einem Verhältnis auf Basis der beabsichtigten Zusammensetzung des keramischen Materials unter Druck zu einem keramischen Material gesintert wird.

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Revendications

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1. Substrat constitué d'un matériau céramique, caractérisé en ce que ledit matériau contient 44 à 47% en atomes de Al, 31 à 39% en atomes de O, 8 à 13% en atomes de C et 8 à 12% en atomes de N.
2. Substrat selon la revendication 1, caractérisé en ce que la composition du composant principal du matériau correspond à la formule $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$.
3. Matériau céramique, caractérisé en ce que ledit matériau contient 44 à 47% en atomes de Al, 31 à 39% en atomes de O, 8 à 13% en atomes de C et 8 à 12% en atomes de N.
4. Matériau céramique selon la revendication 3, caractérisé en ce que la composition du composant principal du matériau correspond à la formule $\text{Al}_{28}\text{O}_{21}\text{C}_6\text{N}_6$.
5. Procédé pour fabriquer un matériau céramique selon la revendication 3 ou 4, caractérisé en ce que le procédé comporte les étapes suivantes:
 - a) le préchauffage d'un mélange constitué de Al_2O_3 , de Al_4C_3 et de AlN dans un rapport basé sur la composition voulue du matériau céramique,
 - b) le broyage jusqu'à une poudre du produit préchauffé ainsi formé,
 - c) le frittage de la poudre de manière à constituer un matériau céramique.
6. Procédé selon la revendication 5, caractérisé en ce que le préchauffage se déroule dans la gamme de températures comprise entre 1500 et 1700°C, et en ce que le frittage se déroule dans la gamme de températures comprise entre 1700 et 1900°C.
7. Procédé pour fabriquer un matériau céramique selon la revendication 3 ou 4, caractérisé en ce qu'un mélange constitué de Al_2O_3 , de Al_4C_3 et de AlN dans un rapport basé sur la composition voulue du

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matériau céramique est fritté sous pression de manière à constituer ledit matériau céramique.

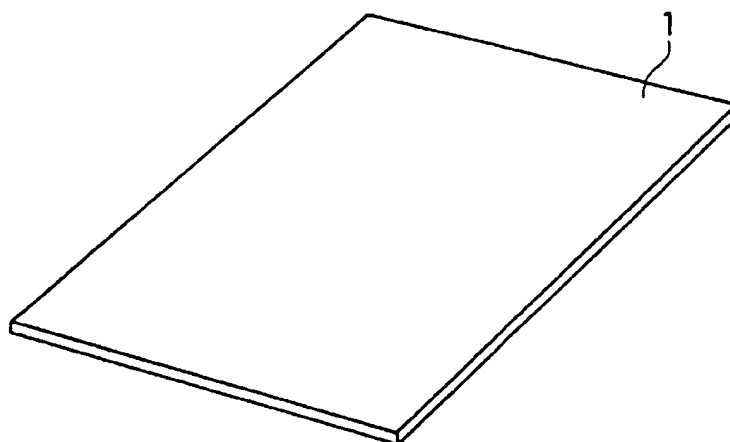


FIG.1

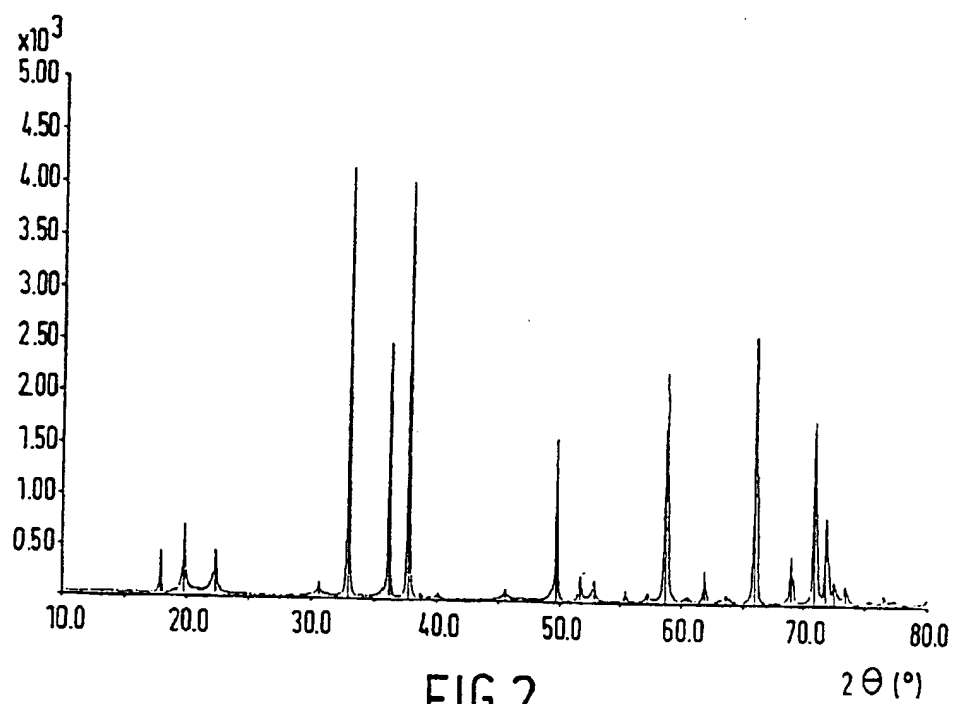


FIG.2